318RTS

10/518030

DT05 Rec'd PCT/PTO 15 DEC 2004

SPECIFICATION

Method of Forming Dielectric Filler-Containing Polyimide Coating on Metallic Material, Method of Manufacturing Copper Clad Laminate for Forming Capacitor Layer for Use in Printed Wiring Board, And Copper Clad Laminate Obtained through the Manufacturing Method

Technical Field

The present invention relates to a method of forming a dielectric filler-containing polyimide coating on a metallic material such as copper, method of manufacturing a copper clad laminate for forming a capacitor layer for use in a printed wiring board, and copper clad laminate obtained through the manufacturing method.

Background Art

In these years, it has become general practice that a capacitor structure is formed by using a copper clad laminate in a printed wiring board, in particular, in the internal layer portion of a multilayer printed wiring board, in a manner similar to that in circuit shape formation, and the capacitor structure thus formed is utilized as a built-in capacitor. The formation of a capacitor structure in the internal layer portion of a multilayer printed wiring board has permitted omitting the capacitors arranged on the external layer surface, and hence the miniaturization and high densification of the external layer circuits has become possible so that the number of the parts mounted on the surface is reduced and the production of a wiring board provided with fine pitch circuits becomes easier.

A capacitor structure is produced by use of a copper clad laminate as follows: a double-sided copper clad laminate comprising respective copper

foil layers on both sides and a dielectric layer interposed therebetween is used, the copper foil layers on both sides are subjected to etching processing to form desired shapes of capacitor electrodes, and the capacitor structure having the dielectric layer sandwiched by the capacitor electrodes on both side is formed in a target position.

The capacitor is demanded to have an electric capacity as large as possible as a fundamental quality thereof. The capacity (C) of a capacitor is derived from the formula $C=\varepsilon\varepsilon_0(A/d)$ (ε_0 is the dielectric constant of vacuum). Accordingly, for the purpose of increasing the capacity of a capacitor, any one of the following procedures has only to be adopted: <1> the surface area (A) of the capacitor electrode is made larger, <2> the thickness (d) of the dielectric layer is made thinner, and <3> the specific dielectric constant (ε) of the dielectric layer is made larger.

However, as far as the surface area (A) described above in <1> is concerned, it is hardly possible to make the area of the capacitor electrode larger in a certain constrained area of a printed wiring board because a printed wiring board is demanded to be lighter and more compact in conformity with the recent trend that electronic and electric appliances are being made lighter and more compact. As for the thickness (d) of the dielectric layer to be made thinner as described above in <2>, if the dielectric layer contains a skeletal material such as glass cloth as represented by prepreg, a limit is given to the formation of a thinner layer by the presence of the skeletal material. On the other hand, if the skeletal material is merely omitted while using a conventional dielectric layer constituting material, an inconvenience occurs that a copper layer is destructed in a portion of the dielectric layer where the copper foil is removed by etching, through the shower pressure of the etching solution that is used in etching for forming a capacitor electrode. In view of these circumstances, it has become general to adopt a procedure in which the

specific dielectric constant (ε) of the dielectric layer is made larger as described above in <3>.

In other words, the increase of the electric capacity of a capacitor has been intended to be actualized in the following way: in the construction of the dielectric layer, a skeletal material such as glass cloth is taken to be indispensable and accordingly the skeletal material is made to be an unwoven material so that the skeletal material may be made thinner and hence the thickness of the whole dielectric layer may also be made thinner, and a resin, in which a dielectric filler is dispersed to be contained therein, is used as the material constituting the dielectric layer.

Thus, in addition to a further enlargement of electric capacity of a built-in capacitor, it has been desired, for a dielectric layer, an establishment of a method of manufacturing a copper clad laminate for forming a capacitor layer, which is thin in thickness, excellent in thickness accuracy, and flexible enough to resist showering pressure applied by etching solution used during an etching process.

For manufacturing a copper clad laminate for forming a capacitor layer, which can meet the conditions, it has been considered a technique disclosed in an official gazette of Japanese Patent Application Laid-open No. 2001-15883 in which a dielectric layer containing dielectric filler in polyimide resin is formed on one side of a copper foil through an electrodeposition coating method with the use of a dielectric filler-containing polyimide electrodeposition solution, which contains dielectric filler in a polyimide electrodeposition solution, and additional copper foil is clad to the dielectric layer.

However, forming a polyimide film directly on a copper surface through an electrodeposition coating method with the use of a polyimide electrodeposition solution is much advantageous over an application method

in that a film thickness can be made small, but it is very difficult in reality, and it was also difficult to operate a polyimide electrodeposition itself in a stable manner. Moreover, it is very difficult to disperse particles of dielectric filler powder uniformly in a polyimide film being electrodeposited after the dielectric filler powder is added in a polyimide electrodeposition solution, so that mass production has not been realized in a real operation.

Thus, it has been sought a technology, which enables formation of a dielectric layer excellent in a thickness accuracy with the use of dielectric filler-containing polyimide electrodeposition solution for forming a dielectric for a copper clad laminate employed to form a capacitor.

Disclosure of the Invention

As a result of diligent study, the present inventors adopted a method of forming a dielectric filler-containing polyimide coating on a surface of a metallic material such as copper and a method of manufacturing a copper clad laminate for forming a capacitor layer for use in a printed wiring board, coming up with a provision of nonconventional copper clad laminate.

In a claim, it is recited that "A method of forming a dielectric filler-containing polyimide coating on a metallic material through an electrodeposition coating method with the use of a dielectric filler-containing polyimide electrodeposition solution, said solution being a polyimide electrodeposition solution in which a dielectric filler has been contained, wherein the used as a dielectric filler is a globoid dielectric powder having perovskite structure which is 0.05 to 1.0 μm in an average particle size D_{IA}, 0.1 to 2.0 μm in a weight cumulative particle size D_{50} based on a laser diffraction scattering particle size distribution measurement method, and 4.5 or less in a coagulation degree value represented by D_{50}/D_{IA} where the weight

cumulative particle size D_{50} and the average particle size D_{IA} obtained from an image analysis.".

It has been believed that an electrodeposition coating method for polyimide resin permits formation of uniform and flawless, for example pin-hole free, coating on metals and formation of a uniform coating onto complicated shapes. Hardly dissolved in a solvent, the conventional polyimides were used for conducting an electrodeposition coating in a state of polyamide acid as a precursor to polyimide, and the conventional polyimides were subject to high-temperature heating to be dehydrated and cyclized to form polyimide coating. However, polyamide acid is easily decomposable and unstable. Therefore, it is preferable in the present invention to employ an electrodeposition solution having compositions for an anion electrodeposition coating, in which used a multi-bloc polyimide soluble to pendantcarboxyl-group-containing solvent. Therefore, a polyimide electrodeposition solution of the type is procurable in the market, and some of the commercially available polyimide electrodeposition solutions have excellent properties.

When a polyimide coating is formed on metals with the use of the polyimide electrodeposition solution, electrodeposition properties will vary dependent on the kinds of metals. Thus, it is necessary to prepare polyimide electrodeposition solutions, with the kinds of the metals as a coated object on which polyimide coating is formed taken into consideration. Especially when a polyimide coating is formed, it does not seem uniform and flawless coatings tend to be formed unless the particle size of colloid particles of multi-bloc polyimide in a polyimide electroposition solution. Therefore, it will be necessary to try to miniaturize the colloid particles through, for example increasing the amount of solvent according to the kinds of the electrodeposition polyimide. However, it is necessary to adjust the colloid

particle size in a polyimide electroposition solution to an appropriate range which can keep a balance between a polyimide coating thickness and electrodeposition properties of ultimate goal, because the thickness of a polyimide coating being formed should be taken into consideration.

Further in the present invention, the properties of the polyimide electrodeposition solution should be determined with even the dispersibility of dielectric fillers to be dispersed and mixed in the polyimide electrodeposition solution taken into consideration. However, there is a ceiling to the kinds of polyimide electrodeposition solutions containing multi-bloc polyimide, which allows the state-of-the-art to form on a metallic material a satisfactory polyimide coating, which is uniform and flawless. There is also a ceiling to a preparation range of the composition.

In this connection, the present inventors decided to improve the properties of the particles of the dielectric fillers to insure a good dispersibility of dielectric filler particles in a polyimide electrodeposition solution. The dielectric fillers to be used in the present invention are intended to be present in a dielectric filler-containing polyimide coating in a dispersed manner, serve finally as a dielectric layer of a capacitor, and are used to increase the capacitance of capacitor when the fillers are fabricated into a capacitor configuration. For the dielectric filler, dielectric particles of a compound oxide having a perovskite structure such as $BaTiO_3$, $SrTiO_3$, $Pb(Zr\text{-}Ti)O_3$ (commonly known as PZT), $PbLaTiO_3 \cdot PbLaZrO$ (commonly known as PLZT), and $SrBi_2Ta_2O_9$ (commonly known as SBT).

The powder characteristic of the dielectric filler is such that in the first place the particle size is needed to fall in the range from 0.05 to 1.0 μm. The particle size as referred to here is the average particle size obtained from the image analysis of the scanning electron microscope (SEM) image taken by directly observing the dielectric filler with a SEM; in the dielectric filler, the

individual powder particles mutually form a certain secondary coagulation state so that indirect measurements in which the average particle size is estimated from the values measured with the laser diffraction scattering particle size distribution measurement method, the BET method and the like, cannot be used because the precision is degraded. In the present specification, the particle sizes thus obtained are represented by D_{IA}. Incidentally, in the present specification, the image analysis for the dielectric filler powder observed with a scanning electron microscope (SEM) was made with the use of an apparatus IP-1000PC manufactured by Asahi Engineering Co. Ltd., with which the average particle sizes D_{IA} were obtained by conducting the circular particle analysis under the conditions that the circularity threshold was 10 and the overlap degree was 20.

Furthermore, it is required that the dielectric filler powder is a nearly spherical dielectric powder having perovskite structure which is 0.1 to 2.0 μm in the weight cumulative particle size D_{50} based on the laser diffraction scattering particle size distribution measurement method, and is 4.5 or less in the coagulation degree represented by D_{50}/D_{IA} where the weight cumulative particle size D_{50} and the average particle size D_{IA} obtained from the image analysis are used.

The weight cumulative particle size D_{50} based on the laser diffraction scattering particle size distribution measurement method is the particle size obtained for the weight cumulation of 50% with the laser diffraction and scattering size distribution measurement method; the smaller is the weight cumulative particle size D_{50}, the larger is the fraction of the fine powder particles in the particle size distribution of the dielectric filler powder. In the present invention, this value is required to be 0.1 μm to 2.0 μm. In other words, when the value of the weight cumulative particle size D_{50} is smaller than 0.1 μm, the progress of the coagulation is remarkable so that the below

mentioned coagulation degree cannot be satisfied irrespective as to what production method is applied to produced the dielectric filler powder. On the other hand, when the value of the weight cumulative particle size D_{50} exceeds 2.0 μm, the use thereof as the dielectric filler for use in formation of the built-in capacitor in a printed wiring board, which is an object of the present invention, becomes impossible. In other words, the dielectric layer, used for formation of the built-in capacitor layer, of a double-sided copper clad laminate is usually 10 μm to 25 μm in thickness so that the upper limit becomes 2.0 μm for the purpose of dispersing the dielectric filler uniformly in the above described dielectric layer.

The measurement of the weight cumulative particle size D_{50} in the present invention was conducted as follows: the dielectric filler powder was mixed and dispersed in methyl ethyl ketone, the solution thus obtained was injected for measurement into the circulation device of a laser diffraction scattering particle size distribution measurement apparatus, Micro Trac HRA 9320-X100 (manufactured by Nikkiso Co., Ltd.)

The concept of the coagulation degree utilized here is adopted on the following grounds. The weight cumulative particle size D_{50} value obtained by use of the laser diffraction scattering particle size distribution measurement method can be regarded as different from the actual individual particle sizes of the powder particles directly observed one by one. This is because most of the powder particles constituting a dielectric powder are not so-called monodisperse particles which are completely separated from each other, but are in a aggregation state in which a plurality of powder particles are coagulated. The laser diffraction scattering particle size distribution measurement method can be said to recognize a group of coagulated particles as one particle (coagulation particle) for derivation of the weight cumulative particle size.

On the contrary, because the average particle size D_{IA}, obtained through image processing of the dielectric powder image observed by use of a scanning electron microscope, is directly obtained from the SEM observation image, the primary particles are observed without fail, but the D_{IA} value does not reflect the coagulation state of the powder particles at all.

In view of the above consideration, the present inventors have taken the D_{50}/D_{IA} value as the coagulation degree on the basis of the D_{50} obtained from the laser diffraction scattering particle size measurement method and the average particle size D_{IA} derived from the image analysis. In other words, on the assumption that the copper powder specimens obtained from the same lot make it possible to measure the D_{50} and D_{IA} values with the same precision, the theory described above deduces the prediction that the D_{50} value, reflecting the presence of the coagulation state to the measured value, will take a value larger than the D_{IA} value (in the actual measurement, similar results are obtained).

In this case, the D_{50} value, when the coagulation state of the powder particles of the dielectric filler powder is absolutely absent, approaches the D_{IA} value without limit so that the coagulation degree of the D_{50}/D_{IA} value approaches unity. Thus, at the stage when the coagulation degree takes a value of unity, the powder can be said to be the monodisperse powder in which the coagulation state of the powder particles is absolutely absent. Actually, however, some cases show the coagulation degrees smaller than unity. From the theoretical viewpoint, the coagulation degree does not take a value smaller than unity in the case involving a perfect sphere, but actually the powder particles are not perfect spheres so that the coagulation value smaller than unity may be obtained.

In the present invention, the coagulation degree of the dielectric filler powder is required to be 4.5 or lower. If the coagulation degree exceeds 4.5,

the level of the mutual coagulation between the individual particles of the dielectric filler powder becomes too high so that the uniform mixing of the dielectric filler powder with the above described binder resin becomes difficult.

Even if any production method of the alkoxide method, the hydrothermal synthesis method, the oxalate method and the like is adopted as the production method of the dielectric filler, a certain coagulation state is inevitably formed, and accordingly such dielectric filler powder that does not satisfy the above described coagulation degree is possibly generated. Particularly, in the case of the hydrothermal synthesis method that is a wet method, the coagulation state formation tends to be generated. In this connection, it is possible to make the coagulation state of the dielectric filler powder attain the above described range of coagulation degree, by conducting a disintegration treatment in which the powder in a coagulation state is disintegrated into individual powder particles.

If the object is the mere disintegration operation, the following various means capable of disintegration can be applied: a high energy ball mill, a high speed conductor collision airflow disintegrator, a collision disintegrator, a gauge mill, a medium-stirring disintegrator, a high hydraulic pressure disintegrator and the like. On the one hand, for the purpose of ensuring the mixability and dispersibility between the dielectric filler powder and the binder resin, it is necessary to take account of the below described viscosity reduction of the dielectric filler containing resin solution. For the purpose of reducing the viscosity of the dielectric filler containing resin solution, it is required that the dielectric filler powder be made small in specific surface area and smooth. Accordingly, the disintegration method, even if capable of disintegration, should not be a disintegration method which, while

disintegration, damages the surface of the powder particles and increases the specific surface area thereof.

As a result of the diligent research performed by the present inventors on the basis of such understanding, two methods have been found to be effective. The fact common to these two methods is that the two methods are sufficiently capable of disintegration in such a way that the contact of the powder particles of the dielectric filler powder onto the parts of the inner wall portion of the apparatus, stirrer blades, disintegration medium and the like, is suppressed to occur to the least extent so that the mutual collision between the coagulated powder particles is made to occur. In other words, the contact onto the parts of the inner wall portion of the apparatus, stirrer blades, disintegration medium and the like leads to damaging the surface of the powder particles, increasing the surface roughness thereof and degrading the sphericity thereof, and hence the contact is prevented. Thus, a method can be adopted in which by making the mutual collision of the power particles occur to a sufficient extent, the powder particles in the coagulation state are disintegrated, and concurrently the surface of the powder particles can be made smooth.

One of the two methods disintegrates the dielectric filler powder in a coagulation state by means of a jet mill. The "jet mill" as referred to here is an apparatus in which a high speed air flow is used, the dielectric filler powder is placed in the high speed air flow, and the mutual collision between the powder particles in the high speed air flow leads to the disintegration operation.

Additionally, a slurry, in which the dielectric filler powder in a coagulation state is dispersed in a solvent capable of maintaining the stoichiometry of the powder, is subjected to the disintegration treatment in which a fluid mill taking advantage of centrifugal force is used. The use of

"the fluid mill taking advantage of centrifugal force" as referred to here makes the slurry flow in a high speed so as to depict a circular orbit, and the centrifugal force thus generated makes the coagulated powder particles collide with each other so that the disintegration operation is performed. Thus, the slurry brought to completion of the disintegration is washed, filtered and dried, and consequently the dielectric filler powder brought to completion of the disintegration operation is obtained. In the above described method, the coagulation degree can be adjusted and the powder surface of the dielectric filler powder can be purposefully made smooth.

The above-described polyimide electrodeposition solution and dielectric filler are mixed to provide a dielectric filler-containing polyimide electrodeposition solution. It is preferable if the mixing ratio of the polyimide electrodeposition solution and dielectric filler is, as described in the claims, determined to make the content of the dielectric filler in the polyimide electrodeposition solution fall within the range of 50g/L to 350g/L.

When the content of the dielectric filler is less than 50g/L, a dielectric constant in a capacitor composed is too low to meet the relative dielectric constant 20, which is currently required in the market. When the content of the dielectric filler exceeds 350g/L, the content of a polyimide resin in a dielectric filler-containing polyimide coating being formed is too low to undermine the adhesiveness to a copper foil being bonded to the coating, thereby making a formation of a capacitor difficult.

Additionally, it is preferable to use barium titanate as the dielectric filler, among the composite oxides having perovskite structure, at the present stage, in consideration of the production precision as a powder. As the dielectric filler in this case, either calcined barium titanate or uncalcined barium titanate can be used. When a high dielectric constant is intended to be attained, it is

preferable to use calcined barium titanate; according to the quality of design for the printed wiring board product, any of these two can be used selectively.

Additionally, furthermore, it is most preferable that the dielectric filler of barium titanate has cubic crystal structure. Barium titanate has cubic and tetragonal crystal structures; the dielectric filler of barium titanate having cubic crystal structure stabilizes the dielectric constant value of the finally obtained dielectric layer as compared to the case where the dielectric filler of barium titanate having only the tetragonal crystal structure is used. Thus, it can be said that it is necessary to use a barium titanate powder that has simultaneously at least both cubic and tetragonal crystal structures.

By employing the above-described dielectric filler-containing polyimide electrodeposition solution to form a dielectric filler-containing polyimide coating on a surface of a copper material through an electrodeposition coating method, the dielectric filler in the dielectric filler-containing polyimide coating is not unevenly distributed but uniformly dispersed even on a copper material, and the dielectric filler-containing polyimide coating per se also has a smooth surface and uniform film thickness, thus being flawless one.

Further, as recited in a claim, adoption of "A method of forming a dielectric filler-containing polyimide coating on a metallic material through an electrodeposition coating method with the use of a dielectric filler-containing polyimide electrodeposition solution, said solution being a polyimide electrodeposition solution in which a dielectric filler has been contained, wherein the method comprising the steps of: forming on a copper material a metallic seed layer of either nickel or cobalt; and forming on a surface of said copper material a dielectric filler-containing polyimide coating through an electrodeposition coating method with the use of a dielectric filler-containing polyimide electrodeposition solution, said solution containing a dielectric powder as a dielectric filler, said dielectric powder having perovskite structure

which is 0.05 to 1.0 μm in an average particle size D_{IA}, 0.1 to 2.0 μm in a weight cumulative particle size D_{50} based on a laser diffraction scattering particle size distribution measurement method, and 4.5 or less in a coagulation degree value represented by D_{50}/D_{IA} where the weight cumulative particle size D_{50} and the average particle size D_{IA} obtained from an image analysis." enables to further improve the uniformity of film thickness of the dielectric filler-containing polyimide coating on a metallic material.

The method of forming a dielectric filler-containing polyimide coating is different from the above-described method of forming a dielectric filler-containing polyimide coating in that a metallic seed layer of either nickel or cobalt should be formed on a metallic material preliminarily, and that a dielectric filler-containing polyimide coating should be formed on a surface of the copper material. In regard to the other aspects, the methods are common, and to avoid repeated description, only a formation of a seed layer of a different metal is discussed. The provided on the metallic layer is a very thin metallic layer of either nickel or cobalt, which exerts excellent electrodeposition properties when an eledctrodeposition coating method is employed. This metal layer is referred to as a metallic seed layer in the specification. In formation of a metallic seed layer onto a surface of a metallic material, various methods such as an electrolytic method and a dry spinning method including a sputtering evaporation method can be adopted, and there is no specific limitation.

The metallic seed layer enables formation of an extremely good polyimide coating even on a surface of a copper foil where formation of a polyimide coating through an electrodeposition coating method has been allegedly difficult. Accordingly, the dielectric filler-containing polyimide coating to be formed finally in the present invention will have an extremely

low possibility of causing any defect, thereby enabling the uniformity of a film thickness to be improved dramatically.

The above-described method of forming a dielectric filler-containing polyimide coating on a metallic material allows dielectric fillers to be uniformly dispersed with no uneven distribution in the dielectric filler-containing polyimide coating, thereby enabling local variation in dielectric constant on a workable-size plane to be decreased. Since the dielectric filler-containing polyimide coating per se has a smooth surface and a uniform film thicknes, electrode materials such as a copper foil to be bonded to the dielectric filler-containing polyimide coating are likely to provide uniform adhesiveness when a capacitor is formed, leading to a manufacturing defect-free product. Adoption of the formation method of a dielectric layer on a surface of a metallic material allows the thickness of the dielectric filler-containing polyimide coating as a dielectric layer to be adjusted in a flexible manner, thereby providing as a result a product having both an excellent electric capacity and a high capacitor quality.

The above-described technical idea of the method of forming a dielectric layer on a surface of a metallic material is applicable to a method of manufacturing a copper clad laminate for forming a capacitor layer in a printed wiring board. Specifically, it is recited in a claim "A method of manufacturing a copper clad laminate for forming a capacitor layer for use in a printed wiring board, said copper clad laminate having a layered structure consisting of a first copper foil, a dielectric filler-containing polyimide dielectric layer, and a second copper foil, comprising the steps of: forming a metallic seed layer of either nickel or cobalt on a surface of a first copper foil; employing a copper foil having a dielectric filler-containing polyimide coating and a copper foil having a polyimid thin film being a polyimide thin film formed on one side of said second copper foil, said dielectric filler-containing

polyimide coating having a dielectric filler-containing polyimide coating formed on a surface of said metal seed layer through an electrodeposition coating method with the use of a dielectric filler-containing polyimide electrodeposition solution, said dielectric filler-containing polyimide electrodeposition solution being prepared through mixing a polyimide electrodeposition solution and a dielectric powder, as a dielectric filler, having a perovskite structure which is 0.05 to 1.0 μm in an average particle size D_{IA}, 0.1 to 2.0 μm in a weight cumulative particle size D_{50} based on a laser diffraction scattering particle size distribution measurement method, and 4.5 or less in a coagulation degree value represented by D_{50}/D_{IA} where the weight cumulative particle size D_{50} and the average particle size D_{IA} obtained from an image analysis; and laminating a surface of the dielectric filler-containing polyimide coating of said copper foil having a dielectric filler-containing polyimide coating and a surface of the polyimide thin film of said copper foil having a polyimide thin film in a manner that both the surfaces come into contact with each other.".

A flow of the manufacturing method is schematically shown in Fig. 1. Specifically speaking, the figure shows an extremely schematic cross-section for better understanding, and the thickness and size have not been reflected truthfully in terms of the values of the product really practiced. Since the basic idea is common with that of the above-described method of forming a dielectric filler-containing polyimide coating on a surface of a metallic material, only a manufacturing procedure of a copper clad laminate will be described.

Description will be made below in connection with the manufacturing method with reference to Fig. 1. A dielectric filler-containing polyimide coating **2** is formed on a surface of a first copper foil **CF1** to provide a copper foil **3** with a dielectric filler-containing polyimide coating. A dielectric filler-

containing polyamide electrodeposition solution as employed for forming the dielectric filler-containing polyimide coating **2** is a mixture, where a dielectric powder was added to a polyimide electrodeposition solution and uniformly mixed. The dielectric powder is substantially spherical and has perovskite structure which is 0.05 to 1.0 μm in an average particle size D_{IA}, 0.1 to 2.0 μm in a weight cumulative particle size D_{50} based on a laser diffraction scattering particle size distribution measurement method, and 4.5 or less in a coagulation degree value represented by D_{50}/D_{IA} where the weight cumulative particle size D_{50} and the average particle size D_{IA} obtained from an image analysis.

Then, the dielectric filler-containing polyamide electrodeposition solution is employed to provide a copper foil **3** with a dielectric filler-containing polyimide coating, on which copper foil has been formed the dielectric filler-containing polyimide coating **2** through an electrodeposition coating method.

In the meantime, a polyimide thin film **4** having a final thickness of 1-3 μm is to be left on one surface of the second copper foil **CF2**, and solvent removal and resin flow, which both occur during drying and press processes, are taken into consideration before manufacturing a copper foil **5** with a polyimide thin film having a thickness of twice or three times of a target thickness. In this instance, a polyimide electrodeposition solution not containing the said dielectric filler is employed to form, on one side of the second copper foil **CF2** through an electrodeposition coating method, a polyimide thin film **4** having a thickness of twice or three times of a final thickness. The polyimide thin film **4** will operate as a binder when bonded with the below-mentioned dielectric filler-containing polyimide coating **2**. When a final polyimide thin film **4** after a press processing is of less than 1 μm, an uneven adhesion surface of the copper foil will be hard to be coated sufficiently, and when the polyimide thin film **4** is of 3 μm or more, the

dielectric constant of a dielectric layer to be finally constituted will decrease remarkably because any dielectric filler is not contained in the polyimide thin film **4** per se.

The copper foil **3** with a dielectric filler-containing polyimide coating and the copper foil **5** with a dielectric filler-containing polyimide thin film, both obtained in the manner as described above are disposed face to face so that the dielectric filler-containing polyimide coating **2** of the copper foil **3** and the polyimide thin film **4** of the copper foil **5** with a polyimide thin film come into contact with each other and are superposed for lamination to provide a copper clad laminate for use in formation of a capacitor layer in a printed wiring board having layers consisting of a first copper foil **CF1**/a dielectric filler-containing polyimide dielectric layer **6**/a second copper foil **CF2**.

Further in another claim, it is recited "a method of manufacturing a copper clad laminate for forming a capacitor layer for use in a printed wiring board, said copper clad laminate having a layered structure consisting of a first copper foil, a dielectric filler-containing polyimide dielectric layer, and a second copper foil, comprising the steps of: forming a metallic seed layer of either nickel or cobalt on a surface of a first copper foil; employing a copper foil having a dielectric filler-containing polyimide coating and a copper foil having a polyimid thin film being a polyimide thin film formed on one side of said second copper foil, said dielectric filler-containing polyimide coating having a dielectric filler-containing polyimide coating formed on a surface of said metal seed layer through an electrodeposition coating method with the use of a dielectric filler-containing polyimide electrodeposition solution, said dielectric filler-containing polyimide electrodeposition solution being prepared through mixing a polyimide electrodeposition solution and a dielectric powder, as a dielectric filler, having a perovskite structure which is 0.05 to 1.0 μm in an average particle size D_{IA}, 0.1 to 2.0 μm in a weight cumulative particle size

D_{50} based on a laser diffraction scattering particle size distribution measurement method, and 4.5 or less in a coagulation degree value represented by D_{50}/D_{IA} where the weight cumulative particle size D_{50} and the average particle size D_{IA} obtained from an image analysis; and laminating a surface of the dielectric filler-containing polyimide coating of said copper foil having a dielectric filler-containing polyimide coating and a surface of the polyimide thin film of said copper foil having a polyimid thin film in a manner that both the surfaces come into contact with each other". A flow of the manufacturing method thereof is shown in Fig. 2 schematically.

The method of manufacturing a copper clad laminate for forming a capacitor layer for use in a printed wiring board is basically the same as the previously discussed method of manufacturing a copper clad laminate for forming a capacitor layer for use in a printed wiring board, however different from each other only in terms of the following aspect. In the first copper foil **CF1**, a metallic seed layer **S** is preliminarily formed onto a surface of the first copper foil **CF1** before formation of a dielectric filler-containing polyimide coating **2**. In the same manner, in the second copper foil **CF2**, a metallic seed layer **S** is preliminarily formed onto a surface of the second copper foil **CF2** before formation of a polyimide coating **4**. Since a method of forming the metallic seed layer **S** is similar to that of forming the above-described dielectric filler-containing polyimide coating onto a metallic material, a description thereof is omitted here for a purpose of avoiding a repetitive description.

Each adhesion surface of the first copper foil **CF1** as well as the second copper foil **CF2,** both surfaces being used in the above-described manufacturing method, is a surface to be used for bonding to the dielectric layer **6** which is normally provided with concavities and convexities so as to bite into the dielectric layer **6** and exert an anchor effect. In the figure, the

adhesion surface is depicted as a surface with attached fine copper particles. As for the copper foil used for a copper clad laminate that constitutes a capacitor layer, it is preferable to use a product in which the nodularized surface of a copper foil is as flat as possible, for the purpose of maintaining the dielectric layer thickness to be uniform. Accordingly, it is preferable to use a very low profile (VLP) copper foil, a rolled copper foil and the like. Incidentally, it is the dielectric filler **F** that is represented by the black points in the figure.

It is indeed possible to manufacture a copper clad laminate by way of using two pieces of the above-described copper foil with a dielectric filler-containing polyimide coating, overlapping each dielectric filler-containing polyimide coating, and pressing them. However, the above method of manufacturing a copper clad laminate made it possible to manufacture a dielectric filler-containing dielectric layer having an optional and uniform thickness, thereby allowing to form an extremely thin dielectric layer. Further, since the dielectric layer of the copper clad laminate according to the present invention is a polyimide coating in which dielectric fillers have been dispersed, it has enough high strength and flexibility which are both features of a polyimide resin, so that the dielectric layer will not be embrittled and prevent any damage caused by a showering of the etching solution conducted at the time of forming a capacitor circuit.

Brief Description of the Drawings

Fig. 1 is a schematic view in cross section showing a production flow of a copper clad laminate for use in formation of a capacitor layer in a printed wiring board. Fig. 2 is a schematic view in cross section showing a production flow of a copper clad laminate for use in formation of a capacitor layer in a printed wiring board. And Fig. 3 is an image of a copper clad

laminate for use in formation of a capacitor layer in a printed wiring board, observed via optical microscope.

Best Mode for Carrying Out the Invention

Description of the present invention is now be made below by way of manufacturing a copper clad laminate for forming a capacitor layer for use in a printed wiring board.

Example 1: In the present example, a copper clad laminate **1** for forming a capacitor layer for use in a printed wiring board was manufactured based on a production flow shown in Fig. 1. In the example, a very low profile (VLP) with a nominal thickness of 35μm was employed as a first copper foil **CF1**.

In advance of forming a dielectric filler-containing polyimide coating **2** on a surface of the first copper foil **CF1**, an acid pickling treatment and electrolytic degreasing treatment were conducted for cleaning the surface of the first copper foil **CF1** in a step of (a-1) in Fig. 1. The acid pickling treatment was carried out with the first copper foil **CF1** immersed for 1 minute in a sulphuric acid solution having a liquid temperature of 25C° and concentration of 1M, and then the first copper foil **CF1** was rinsed with water.

Subsequently, an alkaline degreasing aqueous solution containing 20g/L of sodium carbonate and 5g/L of trisodium phosphate was employed to degrease for 1 minute, rinse with water, and dry the first copper foil **CF1** under the conditions of liquid temperature of 50 C° and electrolytic current of 5A/dm^2.

Next, description is made with respect to a preparation of a dielectric filler-containing polyimide electrodeposition solution. The employed in the present example was a polyimide electrodeposition solution named Q-ED-22-10 manufactured by Kabushiki Kaisha PI Gijutsu kenkyusho to which 25 wt%

of cyclohexanone had been added and of which colloidal particle size had been adjusted.

Then, barium titanium powder which is a dielectric filler **F** having below-mentioned powder properties was mixed and dispersed in the polyimide electrodeposition solution. The mixing ratio was adjusted so that the barium titanium accounts for 80wt% of solid content of polyimide in the above-described dielectric filler-containing polyimide electrodeposition solution.

<u>Powder characteristic of the dielectric filler powder</u>

Average particle size (D_{IA})	0.25 μm
Weight cumulative particle size (D_{50})	0.5 μm
Coagulation degree (D_{50}/D_{IA})	2.0

With the dielectric filler-containing polyimide electrodeposition solution manufactured in a manner as described above, dielectric filler-containing polyimide coating **2** was formed on an adhesion surface of the first copper foil **CF1** through an electrodeposition coating method. As conditions of the electrodeposition coating in this case, the liquid temperature of dielectric filler-containing polyimide electrodeposition solution was set to 25C°, the first copper foil **CF1** should be an anode and a stainless plate should be a cathode. Then, direct current of 5V was applied and electrolysis was performed for 6 minutes to have both polyimide resin and dielectric filler **F** electrtodeposited simultaneously on the copper foil surface, thereby forming a dielectric filler-containing polyimide coating **2** having a thickness of about 8μm, and this coating was rinsed with water.

Finally, drying treatment was carried out with the coating **2** held in an atmosphere of 120C° for 30 minutes. Further the atmosphere was raised to 180C° and the coating **2** was held therein for 30 minutes for drying purpose.

Thus, a copper foil **3** with a dielectric filler-containing polyimide coating as shown in (a-2) in Fig. 1 was manufactured.

At the same time, in forming a second copper foil **CF2**, a copper foil identical to the first copper foil **CF1** was employed, and the copper foil was subjected to acid pickling and degreasing treatments in a step of (b-1) in Fig. 1 in a manner similarly to the above described one. Then, it was rinsed with water and dried, and thereafter the above-described polyimide electrodeposition solution free of dielectric filler was employed to form, on an adhesion surface, a polyimide thin film **4** having a thickness of 10μm so that the second copper foil **CF2** would have a final thickness of about 2-3μ. Finally, drying was carried out with the thin film **4** held in an atmosphere of 120C° for 30 minutes as described above. Further the atmosphere was raised to 180C° and the thin film **4** was held therein for 30 minutes for drying purpose. Thus, a copper foil **5** with a dielectric filler-containing polyimide thin film as shown in (b-2) in Fig. 1 was manufactured.

The obtained coating **2** of the copper foil **3** with a dielectric filler-containing polyimide coating and the thin film **4** of a copper foil **5** with a dielectric filler-containing polyimide thin film were made opposed to each other and laminated as shown in Fig. 1(c), thereby a copper clad laminate **1** for forming a capacitor layer for use in a printed wiring board was manufactured. As the lamination conditions, it was provided that a pressing pressure should be 5kg/cm^2, pressing temperatures should be 250C° for a first 30 minutes and be 300C° for another 30 minutes after the temperature was raised.

Fig. 3 shows a cross section of the copper clad laminate **1** for forming a capacitor layer for use in a printed wiring board thus obtained, which was observed with an optical microscope. The thickness of a dielectric layer **6**, which was formed through laminating the dielectric filler-containing polyimide coating layer **2** and the polyimide thin film **4**, is 10μm on average,

and it will be understood the dielectric layer **6** has a very uniform thickness as Fig. 3 shows clearly.

The first copper foil **CF1** and the second copper foil **CF2**, provided on each face of the copper clad laminate **1** thus manufactured were conditioned with respect to the surface, and dry films were laminated both on the conditioned faces to form etching resist layers. Then, a capacitor circuit was exposed and developed on the etching resist layers to form etching patterns. Thereafter, a circuit etching was effected by the use of copper chloride etching solution, and etching resist layers were stripped to prepare a capacitor circuit. During the etching step, no damages due to a showering pressure of the etching solution occurred to the dielectric layer **6**, and a printed wiring board was provided in a good condition.

Measurement result of the specific inductive capacity of the dielectric layer **6** constituting the capacitor circuit indicated an excellent value of ε = 24.7, which taught a capacitor with a large electric capacity had been provided.

Example 2: The present example describes manufacture of a copper clad laminate **1'** for forming a capacitor layer for use in a printed wiring board based on a production flow shown in Fig. 2. In the present example, a very low profile (VLP) with a nominal thickness of 35μm was employed as a first copper foil **CF1**, as in the case of Example 1.

The steps carried out at the stage in Fig. 2 (a-1) which include acid pickling and degreasing treatments are the same as those done in Example 1. On completion of a degreasing treatment, a nickel metallic seed layer **S** as shown in Fig. 2 (a-2) was provided, and then a dielectric filler-containing polyimide coating **2** was formed on the surface of the first copper foil **CF1**

as shown in Fig. 2 (a-3) to prepare a copper foil **3** with a dielectric filler-containing polyimide coating. As to formation steps for a dielectric filler-containing polyimide coating **2** after provision of a metallic seed layer **S** are the same as done in Example 1.

Therefore, only a method of forming a nickel metallic seed layer **S** is described here. In this Example, a nickel layer of about 100Å was formed as a metallic seed layer **S** with the use of watts nickel bath containing 240g/L of nickel hexahydrate sulfate, 45g/L of nickel hexahydrate chloride, and 30g/L of boric acid for electrodeposition for 1 second under the conditions of pH5, liquid temperature of 55C°, and current density of 2A/dm^2.

At the same time, in forming a second copper foil **CF2**, a copper foil identical to the first copper foil **CF1** was employed, and the copper foil was subjected to acid pickling and degreasing treatments in a step shown in Fig. 2 (b-1) in a manner similarly to the above described one. Then, it was rinsed with water and dried before formation of a metallic seed layer S as shown in Fig. 2 (b-1), and thereafter the above-described polyimide electrodeposition solution free of dielectric filler was employed to form, on an adhesion surface, a polyimide thin film **4** having a thickness of 10μm so that the second copper foil **CF2** would have a final thickness of about 2-3μm. Finally, drying was carried out with the thin film **4** held in an atmosphere of 120C° for 30 minutes as described above. Further the atmosphere was raised to 180C° and the thin film **4** was held therein for 30 minutes for drying purpose. Thus, a copper foil **5'** with a dielectric filler-containing polyimide thin film as shown in Fig. 1 (b-3) was manufactured.

The obtained coating layer **2** of the copper foil **3'** with a dielectric filler-containing polyimide coating and the thin film **4** of a copper foil **5'** with a dielectric filler-containing polyimide thin film were made opposed to each other and laminated as shown in Fig. 2 (c), thereby a copper clad laminate **1'**

for forming a capacitor layer for use in a printed wiring board was manufactured. Since the lamination conditions in this case are identical to those in Example 1, a description is omitted here to avoid a duplicated description.

When a cross section of the copper clad laminate **1'** for forming a capacitor layer for use in a printed wiring board thus obtained was observed with an optical microscope, the cross section provides a similar state to that shown in Fig. 3 because the metallic seed layer **S** is too thin to be observed. For this reason, presentation of a cross section of the copper clad laminate **1'** observed via an optical microscope is omitted. However, in this Example, the thickness of a dielectric layer **6**, which was formed through laminating the dielectric filler-containing polyimide coating layer **2** and the polyimide thin film **4,** is 9.5μm on average, and it will be understood the dielectric layer **6** is very smooth and has a uniform thickness.

The first copper foil **CF1** and the second copper foil **CF2**, provided on each face of the copper clad laminate **1'** thus manufactured were conditioned with respect to the surface, and dry films were laminated both on the conditioned faces to form etching resist layers. Then, a capacitor circuit having a size of 1cm x 1cm was exposed and developed on the etching resist layers to form etching patterns. Thereafter, a circuit etching was effected by the use of copper chloride etching solution and etching resist layers were stripped to prepare a capacitor circuit. During the etching step, no damages due to a showering pressure of the etching solution occurred to the dielectric layer **6**, and a printed wiring board was provided in a good condition.

Measurement result of the specific inductive capacity of the dielectric layer **6** constituting the capacitor circuit indicated an excellent value of ε = 33.6, which taught a capacitor with a large electric capacity had been provided.

Industrial Applicability

The method of forming a dielectric filler-containing polyimide coating according to the present invention on a metal surface through an electrodeposition coating method enables a formation of a thin but uniform and smooth dielectric filler-containing polyimide coating, and once this layer is used as a dielectric layer for a capacitor, a higher dielectric constant can be achieved, so that an electric capacitance for a capacitor can be improved and stability in quality can also be improved remarkably owing to few defects. Additionally, application of similar technological idea to manufacture of a copper clad laminate where a dielectric filler-containing polyimide coating is used as a dielectric layer can provide a high-quality constituent material for a capacitor layer used in a printed wiring board.